

# GROWTH AND CHARACTERIZATION OF $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ ALLOYS FOR USE IN HETEROJUNCTION BIPOLAR TRANSISTORS

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## ABSTRACT

This paper intends to serve as an introduction for the following technical reports on research at ISGC institutions related to growth and characterization of  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  alloys. I review the history of electronic and optoelectronic materials and explain why heterojunction bipolar transistors based on these group-IV alloys have great potential in wireless communications applications. I describe the growth methods, the role of strain for device engineering, and optical characterization techniques, especially spectroscopic ellipsometry and photorefectance.

## THE QUEST FOR ELECTRONIC MATERIALS

A quick look at the periodic table of the elements reveals that most elements are either metals or gases and therefore cannot be the basis of a microelectronics technology. In the fourth column, however, we find three elements (diamond, silicon, and germanium) with unusual properties: They are transparent at sufficiently long wavelengths and have a small electrical conductivity, at least at low temperatures. Because of these properties, they are called **insulators** or **semiconductors** (since their electrical conductivity becomes nonzero at elevated temperatures).

These properties can be explained with the nature of their chemical bonding: The four valence electrons (1 s- and 3 p-electrons) of, say, silicon pair up with four electrons of neighboring atoms to form a stable covalent bond. In LCAO theory (linear combination of atomic orbitals), this bond is thought to be made up of s-bonding and p-bonding orbitals, which are formed by the symmetric combination of atomic orbitals. There are also antisymmetric combinations of orbitals, which are known as the s-antibonding and p-antibonding states. For elements in the fourth column, the bonding states (also called valence band) are occupied by valence electrons and the antibonding states (also called conduction band) are empty. This leads to the chemical stability of the solid and their vanishing electrical conductivity. The optical properties are explained by an energy gap (forbidden zone) between the bonding and antibonding states.

In the late 1940s, Bardeen and Brattain realized that the electrical conductivity can be controlled by adding impurity atoms, such as boron or phosphorus, known as dopants. This led to the **invention of the transistor**, which created an industrial revolution. The first transistors were made of germanium, but nowadays conventional electronic circuits are based on silicon. Silicon is a rather lousy electronic material due to the low mobility of electrons (in the conduction band) and holes (missing electrons in the valence band). However, it has a very stable insulating oxide ( $\text{SiO}_2$ , which we also know as glass) and superior mechanical and thermal properties: It is very hard, easy to work with, and has a very high thermal conductivity. Since power consumption and thermal dissipation is the most important prob-

lem in integrated circuits with very high integration (such as computer CPUs or memory chips), silicon has become the material of choice for electronic applications. Discrete germanium transistors were used for high-frequency applications until the 70s. Diamond crystals have never found many applications in microelectronics, since they are rare in nature and difficult to manufacture in large sizes.

Since the early 50s, researchers have been looking for **improved electronic materials**. In 1952, Welker and coworkers at Siemens (Erlangen, Germany) began to study the properties of InSb, AlSb, GaAs, and InP. These materials, known as **compound semiconductors**, consist of elements from the third and fifth column of the periodic table. Since three and five make four electrons per atom on average, these compounds have similar properties as silicon and germanium. A more detailed investigation shows that GaAs has superior electronic properties (with a six times higher mobility than silicon), but it is also brittle, more expensive to manufacture, and very difficult to integrate into high-density circuits. In the late 1980s, Cray Research decided to develop a CPU with 1 GHz clock speed for a supercomputer on GaAs basis. The results were impressive, but the CPU turned out to be so expensive that Cray never sold a single unit. A few days before Christmas in 1990, IBM also decided to disband its GaAs electronics program. Today, GaAs only has a limited range of electronic applications, particularly for simple, high-frequency circuits (microwaves, cellular telephones). Therefore, Lucent Technologies (formerly known as AT&T) is still interested in this material.

Also in the mid-50s, scientists at the RCA laboratories in Princeton, NJ, tried to mix Si, Ge, and diamond to form **semiconductor alloys**. They found that Si and Ge are completely miscible (i.e., solid solutions of arbitrary composition can be produced), but diamond has a very small solubility in Si and Ge, with the exception of the compound SiC containing 50% Si and 50% carbon. Detailed studies of  $\text{Si}_{1-x}\text{Ge}_x$  and compound semiconductor alloys came to the conclusion that, from a fundamental point of view, **semiconductor alloys are rather boring**: Most properties, such as the lattice constant or band gap scale linearly with composition, although small deviations (bowing) are usually found. Large deviations from linearity are interesting, but usually can be explained with a simple argument, for example the crossing of two bands or the mass difference of the ions.

The production of a third type of artificial semiconductors became possible during the 1970s and 80s through advances in epitaxial growth techniques: It is technologically possible to deposit only a few layers of atoms at a time. This allows the growth of artificial sandwich structures called **superlattices**, e.g., repeated growth of Si followed by Ge. If the period of this structure is smaller than the de Broglie wavelength of the electron (typically a few hundred Ångströms), then the electron sees the average properties of this new material rather than those of the individual constituents. The interface between two different materials with different doping levels is known as a **heterojunction** (to distinguish it from the homojunctions found in conventional Si-based diodes and transistors). A thin layer of one material embedded in a different material with a larger band gap is called a **quantum well**.

## OPTOELECTRONICS

Although GaAs failed to displace Si in microelectronics and could only find some niche markets, particularly in high-speed circuits, it had a major impact on our society: The main

difference between Si and GaAs is in their optical properties. It may sound absurd, but low-energy electrons and holes travel at different speeds through the Si crystal and therefore rarely see each other. (In other words: Silicon is an **indirect semiconductor**.) As a result, it is not very probable for electron-hole pairs to recombine or to be created by an incident light wave (photon). In physical terms, the absorption coefficient of Si is small and the lifetime of electron-hole pairs is long. Therefore, Si cannot be used to make semiconductor lasers and crystalline Si has only a limited conversion efficiency in solar cells.

GaAs, on the other hand, is a **direct semiconductor**: The electron and hole states with the lowest excess energy occur at the same region in crystal momentum space. Therefore, the wave functions of electron and hole overlap, which leads to large absorption cross sections and recombination probabilities. Based on this property, it became possible to manufacture efficient semiconductor lasers, photodetectors, and solar cells. These optoelectronic devices found everyday applications in compact disc-players, CD-ROMs, and fiber-optic communication (telephone, cable TV, or the Iowa fiber-optic network linking schools and libraries to the information superhighway).

This optoelectronic technology does have a price, however: It is much more expensive to manufacture GaAs-based devices than those based on Si. Furthermore, the packing density of compound semiconductor circuits is limited, partly due to their high power consumption and the poor qualities of their native oxides. Finally, the GaAs processing steps are not compatible with those of Si, therefore electronic and optoelectronic devices cannot be integrated.

There is a dream, however, the “holy grail” of silicon technology, to somehow modify the properties of Si for optoelectronic applications. It has been suggested that short-period Si/Ge superlattices or  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  alloys may have a direct band gap under certain conditions, which would make the production of semiconductor lasers on Si substrates feasible. While the search for direct Si-based materials is a high-risk endeavor, the payoff would be enormous, if the search was successful. Besides, we expect to find other new technologies along the way. If a direct band gap cannot be found, there may be other applications of  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  alloys in optoelectronics, such as modulators and detectors.[1]

## HETEROJUNCTION BIPOLAR TRANSISTORS AND APPLICATIONS

The fastest transistors[2] presently have a cutoff frequency (switching speed) of almost 200 GHz. These bipolar devices have an n-type InP emitter, a very thin (260 Å) p-type InGaAs base, and an n-type InP collector. The switching speed is related to the transit time through the base, which is affected by three factors: (i) The base needs to be thin. (ii) The use of a heterojunction launches the electron from the InP barrier (emitter) into the InGaAs well (base) and therefore reduces the transit time. (iii) Rather than doping the base, the surrounding barriers are doped with a very thin profile. The carriers leak from the barrier into the well to allow transport leaving behind ionized impurities in the barrier. Thus, the ionized impurity scattering in the base (which is the dominant scattering mechanism) is reduced. The last concept is known as **modulation doping**.

Such transistors are made up of several materials and therefore called **heterojunction bipolar transistors** (HBTs). They are much faster than regular Si bipolar transistors (50 GHz). More recently, the concepts of heterojunctions and modulation doping

have also been transferred to the silicon world.[3, 4, 5] The second material (needed to form a heterojunction) is a  $\text{Si}_{0.7}\text{Ge}_{0.3}$  alloy. SiGe HBTs are somewhat slower (100 GHz) than compound semiconductor HBTs, but they have the advantage of allowing to combine analog high-frequency SiGe HBTs for radio-frequency applications with Si field-effect transistors (CMOS) for digital applications. Using this technology, IBM and Analog Devices demonstrated a 1 GHz, 12 bit, digital-to-analog converter with 2854 SiGe HBTs and 1465 poly-silicon resistors. Even faster (1.8 GHz) converters are currently tested by Analog Devices. Other companies, such as NEC (Kanagawa, Japan) and Daimler-Benz (Ulm, Germany) which dominate the wireless communication markets in Japan and Germany, have had similar success in their SiGe research programs.

It is worth mentioning that conventional Si technology has not been idle while other technologies (SiGe, GaAs) made big progress: Between 1980 and 1990, the cutoff frequencies of Si bipolar transistors increased from less than 10 GHz to almost 50 GHz. Currently, SiGe-based transistors are 10% to 50% faster than the best Si bipolar transistors, but 2 to 6 times slower than the best GaAs devices. Therefore, the potential market for SiGe-devices is getting smaller. Si devices easily meet the requirements for the 2.4 GHz wide local area network (WLAN) and wireless communications markets. GaAs devices, on the other hand, are getting cheaper (less than \$1 for a GaAs HBT Darlington amplifier).

At the International Conference on Semiconductor Physics held in Berlin, Germany, last July, A. W. Wieder, the manager of the computer memory (D-RAM) production of Siemens (Munich, Germany) made the following statements: Industrial semiconductor development looks 10 to 15 years into the future. For example, the development of the 1 GBit D-RAM chip was just completed. Production will begin by about 2005 or 2010. Siemens is currently working on the development of the 4 GBit D-RAM, where no major technological road blocks are expected. He said that basic semiconductor research at universities should not compete with industry, but rather study problems which may become important in 15 to 25 years. If his statements are true, then the current market situation should not affect the direction of our research. Instead, we need to investigate the feasibility of technologies such as those based on SiGe. While some of these technologies will become important in the marketplace, others will not.

## GROWTH

Large semiconductor single crystals (such as Si, Ge, or GaAs) are typically pulled from the melt (Czochralski, Bridgman techniques). The purity of these crystals can be improved by zone refining. Using such techniques, only bulk (i.e., large) crystals can be grown. Since growth is very fast (at least on an atomic scale), it occurs at thermal equilibrium. Unstable or metastable materials (such as diamond) cannot be produced with these techniques. The growth of less common compounds (say, AlSb) can be challenging. It is possible, but quite difficult, to grow semiconductor alloys from the melt. A group in the (former Soviet) Republic of Georgia successfully produced  $\text{Si}_{1-x}\text{Ge}_x$  single crystals for use as solar cells in the Soviet space program.

The heterojunction bipolar transistor techniques described previously can only be produced using **epitaxial techniques**. The word **epitaxy** is taken from the Greek word *taxis*, which means order. It refers to the very slow growth (a few atomic layers per second)

of thin layers (typically 1  $\mu\text{m}$  or less) on a crystalline substrate. The substrate defines the pattern of deposition.

In **molecular beam epitaxy** (MBE), growth occurs in an ultra-high vacuum chamber. The atoms to be deposited are supplied by effusion cells, i.e., a crucible containing the melt of an element. If the temperature of the melt is high (near the evaporation point), then the vapor pressure is high. There is a constant stream of atoms (molecular beam) in all directions. A small hole in the effusion cell allows the molecular beam to reach the growing surface (substrate). The hole can be closed with a shutter. An MBE chamber with Si and Ge effusion cells can be used to produce  $\text{Si}_{1-x}\text{Ge}_x$  alloys, if both shutters are open. Dopants can be supplied with additional cells containing boron or phosphorus. The composition can be controlled by changing the size of the opening or the temperature of the cell. A superlattice or a heterojunction can be grown, if only one shutter is opened at a time.

It is also possible to supply the atoms needed for epitaxial growth in the vapor phase. This is known as **chemical vapor deposition** (CVD) or **vapor phase epitaxy** (VPE). Suitable gases are, for example, silane and germane (similar to methane, but with the carbon atom replaced by Si or Ge), phosphine, or larger metal-organic molecules such as trimethylgallium. The gases are often diluted with an inert carrier gas, usually hydrogen. When the gas molecules are near the substrate, they are cracked, i.e., their chemical bonds are broken, either by a high temperature or some other energy source such as a high-power radio wave.

Both of these techniques operate far from thermal equilibrium. Therefore, it becomes possible to grow not only stable, but also metastable structures. For example, the solubility of carbon in Si and Ge vanishes in the bulk, as mentioned before. However, the surface miscibility is relatively large. Therefore, using epitaxial techniques, it is possible to produce  $\text{Si}_{1-y}\text{C}_y$ ,  $\text{Ge}_{1-y}\text{C}_y$ , and  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  alloys, since the atoms cannot diffuse from the surface into the bulk due to the nonequilibrium growth conditions. Since the growth rates are very slow, it is possible to grow complicated structures, such as quantum wells, superlattices, thin doping spikes, etc. **Liquid phase epitaxy** (LPE) is a third epitaxial technique. It allows some vertical growth control, but operates at or near thermal equilibrium, since the material is grown from the melt.

## STRAIN AND RELAXATION BY FORMATION OF DISLOCATIONS

Every semiconductor has its own characteristic lattice constant (the spacing between the planes of the crystal). While some materials (such as GaAs and AlAs) are pretty well matched in their lattice constants, others are not: The mismatch between Si and Ge is 4% and that between Si and diamond even 50%. This leads to a problem in heteroepitaxy: Defect-free growth requires a deformation of the lattice constant. In *pseudomorphic growth*, where the substrate acts as a template for the growth[3], the in-plane lattice constant of the epitaxial layer is equal to that of the substrate, but the lattice constant along the growth direction is larger or smaller (depending on the lattice mismatch) to minimize the volume change of the epitaxial layer compared to the bulk. This leads to a biaxial distortion of the layer, which requires energy. When the thickness of the epitaxial layer reaches the **critical thickness**, the elastic energy stored in the biaxially strained layer becomes large enough to form **misfit dislocations**: The crystal gives up the favored fourfold coordination at some

lattice sites to reduce the strain. The dislocations can multiply and glide to the surface or to the active device region, where they deteriorate the device performance.

While it is true that too much strain causes dislocations and thus deteriorates device performance, some elastic strain is actually one essential ingredient in the performance enhancements of HBTs. The strain lifts the degeneracies of certain bands. In silicon, for example, there are two types of holes, called the heavy and light hole bands. As can be expected, the heavy hole band has a low mobility and the light hole band a high one. In unstrained Si, both hole bands are degenerate, therefore transport occurs in both bands and the mobility is mediocre. In the IBM design for a high-performance SiGe-based HBT[4], the base consists of a thin p-type Si channel with a tensile strain, which lifts the degeneracy of the hole bands. Since the transport occurs predominantly in the light-hole band, the mobility is larger than in unstrained Si. While tensile strain improves the performance, compressive strain decreases it, since transport would occur in the heavy-hole band.

We have seen that heteroepitaxy (i.e., the epitaxial growth of different semiconductors) has the following advantages: (i) The charge carriers can be launched from the emitter into the base, if the band gaps of the two materials are different, thus reducing the transit time through the base. (ii) By doping the barrier rather than the base, the ionized impurity scattering in the base is reduced. (iii) The mobility in the base can also be improved by choosing the proper strain conditions.

A strained Si base requires a dislocation-free  $\text{Si}_{1-x}\text{Ge}_x$  substrate. Although bulk  $\text{Si}_{1-x}\text{Ge}_x$  can be grown, they are not of sufficient size and quality for high-end devices. Therefore, a  $\text{Si}_{1-x}\text{Ge}_x$  pseudosubstrate is needed. In the IBM design, this pseudosubstrate consists of a thick compositionally graded  $\text{Si}_{1-x}\text{Ge}_x$  layer with a complicated structure. This particular (proprietary) structure dramatically reduces the dislocation density[3].

## THE ROLE OF CARBON

For practical reasons, the base in a SiGe-based HBT should be at least a few hundred Ångströms thick. The critical thickness for Si on  $\text{Si}_{1-x}\text{Ge}_x$  therefore limits the Ge concentration to about 30%. It may be desirable, however, to have layers with a larger Ge content. Therefore, it has been suggested to incorporate carbon into  $\text{Si}_{1-x}\text{Ge}_x$  and form ternary  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  alloys. Because of the lattice constants of Si, Ge, and carbon, one percent of carbon in  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  reduces the strain of about 8% of Ge. Thus, it should be possible, at least in principle, to increase the Ge content to arbitrary values, provided that the additional strain is compensated by a sufficient amount of carbon.

An added benefit of carbon is that it changes the band offsets, i.e., the discontinuities in the conduction and valence bands going from one material to another. These band offsets depend not only on composition, but also on strain.

As mentioned before, the incorporation of C into  $\text{Si}_{1-x}\text{Ge}_x$  is difficult, but possible using epitaxial techniques. As much as 2% to 3% of carbon have been incorporated into Si, Ge, and  $\text{Si}_{1-x}\text{Ge}_x$  alloys. It was found, however, that carbon in  $\text{Si}_{1-x}\text{Ge}_x$  has rather unusual properties: While one would expect that carbon should increase the (indirect) band gap of  $\text{Si}_{1-x}\text{Ge}_x$ , it was actually found to decrease, even after the effects of strain (which always reduces the band gap) were taken into account. A different study by other groups found no surprises for the direct gap of  $\text{Si}_{1-y}\text{C}_y$  alloys: As expected, the direct gap of

$\text{Si}_{1-y}\text{C}_y$  followed a linear interpolation if the effects of strain were properly taken into account. Theory also predicts that the role of C may be different from that of Si and Ge. Clearly, we currently do not understand  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  at all. Therefore, additional investigations need be performed before device designers can even begin to propose  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ -based electronic or optoelectronic devices.

## CHARACTERIZATION

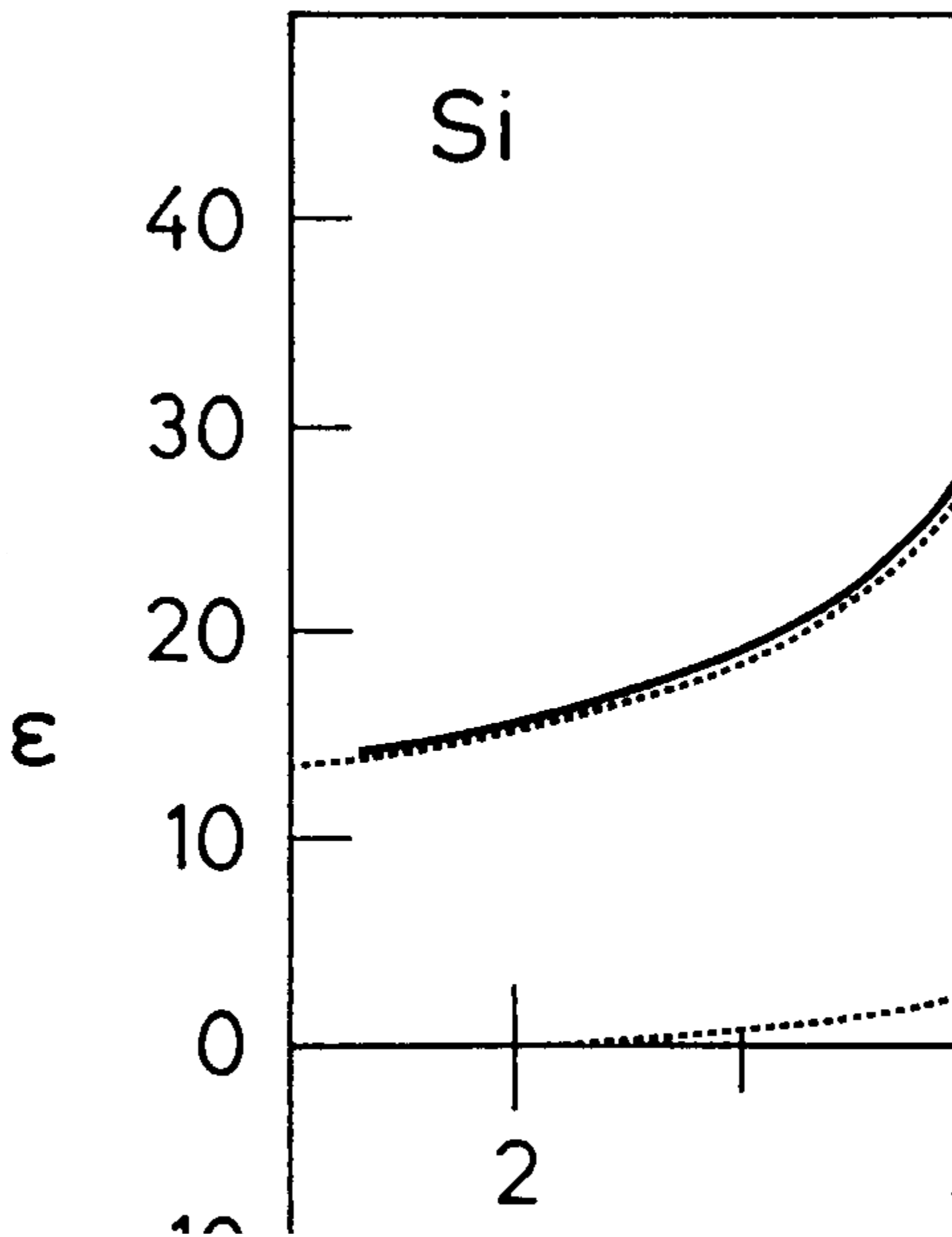
A variety of characterization techniques is employed to study the properties of  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  *in situ* (in the growth chamber during growth) and *ex situ* (after growth). X-ray scattering is typically used to find the lattice constant of the material. Secondary ion mass spectroscopy (SIMS), Rutherford backscattering (RBS), Auger emission spectroscopy (AES), and x-ray photoelectron spectroscopy (XPS) can be used to find the chemical composition of the compound. An iodine-based etch enlarges the dislocations at the surface. The resulting pits can be counted to find the surface dislocation density. More detailed structural information can be found from atomic force microscopy (AFM) or transmission electron microscopy (TEM). Electrical measurements determine the mobility of the material. Raman and Fourier-transform infrared (FTIR) spectroscopy can find information about the energy of lattice vibrations, strain, and defects.

In this work, I focus on optical techniques which are aiming to determine the band structure of a material. Photoluminescence and transmission find the lowest band gap of the material, which happens to be the indirect gap of  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ , but they may also be affected by defects. Other techniques are needed to find the energies of direct optical transitions.

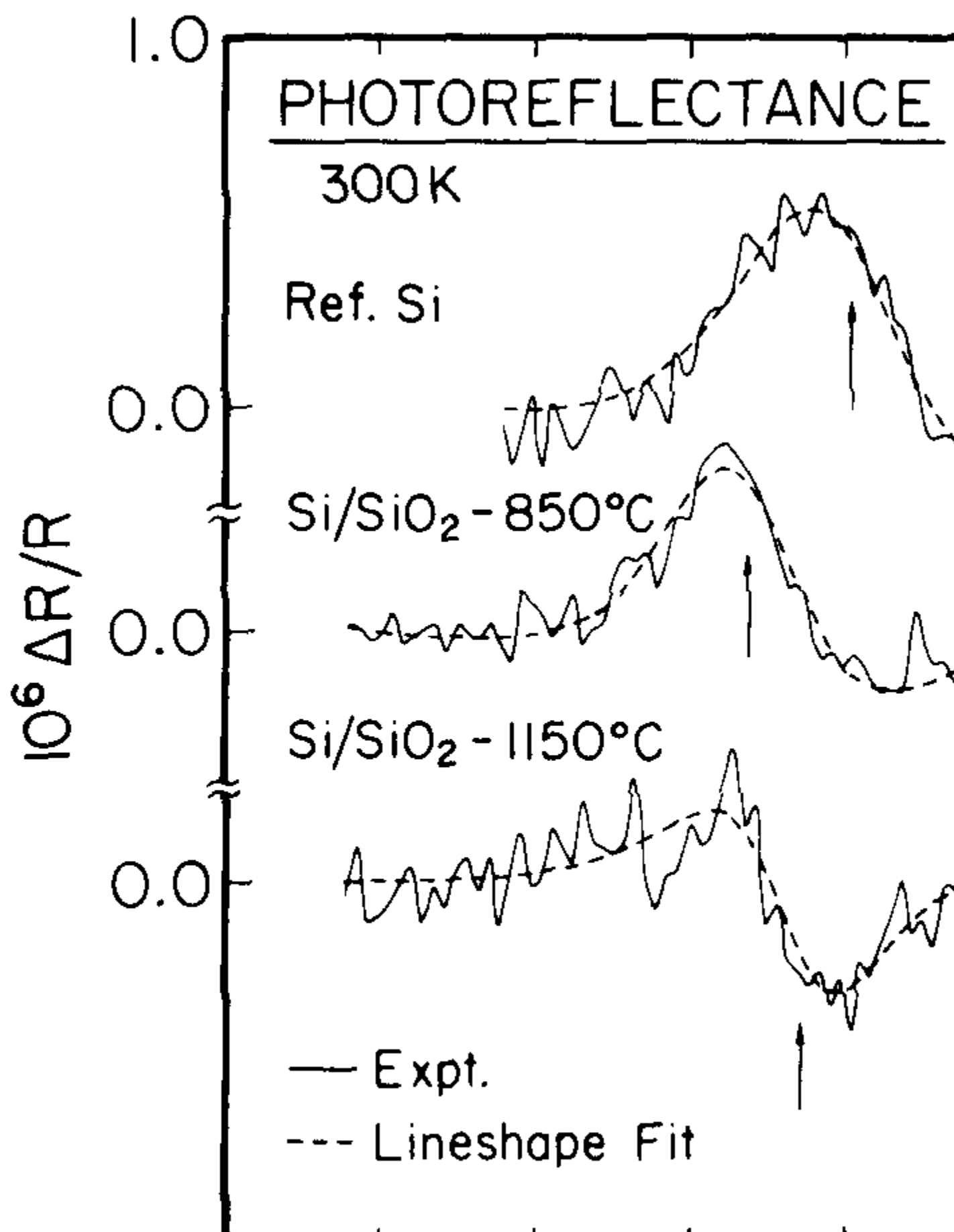
## SPECTROSCOPIC ELLIPSOMETRY

The macroscopic optical response of a material to a monochromatic light wave is determined by the reflection and absorption coefficients. These two real quantities can be combined in one complex number, the complex refractive index. The square of the refractive index is the dielectric function (also complex). If a material is transparent or has a small absorption coefficient, these numbers are best found from transmission-based measurements. If the penetration depth gets smaller than a few hundred Ångströms (when absorption by direct optical transitions becomes important), then transmission measurements become difficult. This is where spectroscopic ellipsometry (SE) becomes useful.

In SE, we measure the change of the state of polarization, when a beam of light is reflected at a surface.[7] Using a simple formula (the complex Fresnel equation), we can find the optical constants listed above from this polarization information. It is obvious that the exact values of the optical constants are very important for the design of optoelectronic devices. If the sample is not a uniform material, but has several buried surfaces, then SE can sometimes determine the thicknesses of the individual layers by analyzing the thin-film interference pattern. By comparison with a database of known materials,[8] SE may also be able to determine the composition and strain of the layers. The measured spectrum is also affected by dislocations, doping levels, uniformity of the layers, etc. A typical dielectric function for pure, bulk Si is shown in Fig. 1.







co-PIs at ISU and UNI were able to find new collaborators at IBM (S. S. Iyer, K. Eberl, and A. P. Powell) and the University of Delaware (J. Kolodzey) who provided samples for optical studies. The following series of papers reports the results of the investigation of the optical properties of materials supplied by these groups, particularly thick relaxed Ge films on Si grown by MBE,  $\text{Si}_{1-y}\text{C}_y$  alloys, and  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  alloys. Future work will include collaborations with V. Dalal's and Gary Tuttle's groups at ISU, J. C. Sturm from Princeton, and K. L. Wang at UCLA. In addition to our current line of research, we will study microcrystalline  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  alloys,  $\text{Si}_{1-x}\text{Ge}_x$  alloys grown on BESOI (back-etched Si on insulator), and the relationship between dislocations and critical point parameters in strained III-V semiconductors.

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